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Research Topics in Explosives - A Look at Explosives Behaviors

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Research Topics in Explosives - A Look at Explosives Behaviors

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Abstract. The behaviors of explosives under many conditions – e.g., sensitivity to inadvertent reactions, explosion, detonation – are controlled by the chemical and physical properties of the explosive materials. Several properties are considered for a range of improvised and conventional explosives. Here we compare these properties across a wide range of explosives to develop an understanding of explosive behaviors. For improvised explosives, which are generally heterogeneous mixtures of ingredients, we identify a range of studies needed to more fully understand their behavior and properties. For conventional explosives, which are generally comprised of crystalline explosive molecules held together with a binder, we identify key material properties that determine overall sensitivity, including the extremely safe behavior of Insensitive High Explosives, and discuss an approach to predicting the sensitivity or insensitivity of an explosive.

1. Introduction

There are many forms of explosives, and each exhibits different behaviors. For example, conventional explosives are designed to be safe to handle and stable for long periods of time while maximizing detonation energy. In contrast, improvised explosives are designed to be easy to make and difficult to detect, with a lower priority on safety and performance. We have studied a range of explosives and their properties for many years, and here we present an evaluation of how material properties govern explosive behaviors for these types of explosives.

In addition to the differences noted above, improvised and conventional explosives have markedly different reaction kinetics under detonation conditions and therefore have different energy release behaviors. This means that methods developed for quantifying the performance of conventional explosives may not be accurate for improvised explosives. We will discuss some of the aspects of improvised explosives that lead to this problem.

Conventional explosives vary in their response to accidental stimuli, with behaviors ranging from violent detonations to very slow combustion (similar to wood). This latter type of explosive may be designated as an Insensitive High Explosive (IHE). We will discuss material properties that determine this behavior, and will present an approach that is being developed to integrate material property

information into a predictive model of explosive sensitivity and violence under hazards situations. Such a model will be helpful in developing new explosives and in characterizing them as IHEs.

2. Improvised Explosives

Improvised explosives have key differences from conventional explosives. One of the most important is shown in Figure 1. Virtually all explosives release energy produced by oxidation of a fuel. In conventional explosives such as 2, 4, 6 trinitrotoluene (TNT), the fuel (carbon in the benzene ring) is in the same molecule as the oxidizer (oxygen on the nitro group). Molecular explosives like TNT (and virtually all conventional explosives) are materials that contain C, H, N and O. They are characterized by high density, very fast reaction and therefore very high power, and very high detonation pressure. Decades of detonation science has been devoted to study of such materials.

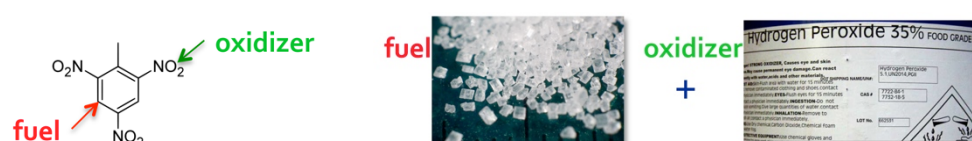


Figure 1. Conventional explosive (left, TNT) and improvised explosive (right, fuel plus hydrogen peroxide).

In contrast, improvised explosives are typically mixtures of a fuel and an oxidizer, which may be solids or liquids. For mixtures involving a solid fuel and / or oxidizer, this generally results in a low density material. The separation of fuel and oxidizer ($\sim 100 \times 10^{-6}$ m vs $\sim 100 \times 10^{-12}$ m for molecular explosives) results in slow reaction rates as mass-transfer rates limit the overall reaction. Therefore improvised explosives are much lower in power than conventional explosives, and have significantly lower detonation pressures. Furthermore the fuel and/or oxidizers generally contain elements beyond those in conventional explosives. These differences mean that methods developed in detonation science of conventional explosives do not always apply to improvised explosives.

2.1. Safety of improvised explosives – an example of thermal instability

As an example of unexpected behavior of an improvised explosive, we consider a mixture of hydrogen peroxide and a fuel. Generally explosives are expected to be stable at room temperature, but with this mixture the thermal stability was called into doubt when analysis by differential scanning calorimetry showed onset of reaction at a very low temperature, as shown in Figure 2. Although the

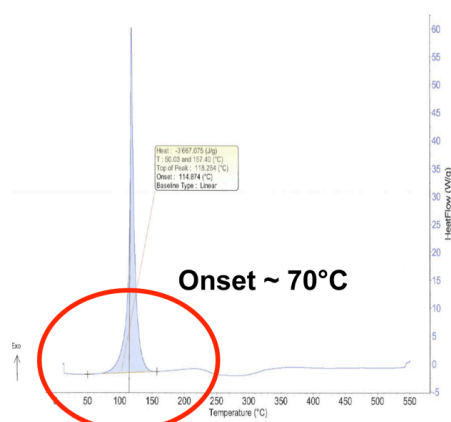


Figure 2. Differential scanning calorimeter analysis of hydrogen peroxide / fuel mixture, at a scan rate of $10^{\circ}\text{C}/\text{min}$.

reaction onset occurred over room temperature, it was sufficiently low that we were concerned about the overall thermal stability of the mixture. Therefore we ran the test shown in Figure 3, in which a sample was held in an insulated container without heating. As shown in Figure 3, the mixture

experienced a runaway reaction after about 40 hours. Self-ignition at room temperature is a graphic example of how improvised explosives are inherently more dangerous than conventional explosives.



Figure 3. Self-heating test for hydrogen peroxide / fuel mixture. A 50-gram sample was placed in a glass bottle sealed by a rubber septum, and the bottle was placed in an insulating foam, with no external heating (left). After approximately 40 hours the mixture exploded, shattering the glass bottle and expelling contents at least 2 meters (right).

2.2. Performance of improvised explosives – key differences with conventional explosives

As described above, explosives produce energy by the oxidation of a fuel. As shown in Figure 1, conventional explosives contain the fuel and the oxidizer in the same molecule; the distance between the oxidizer and fuel moieties is on the order of 10^{-10} m. In contrast, improvised explosives are generally comprised of physical mixtures of solids and / or liquids; for mixtures of solids the mean distance between oxidizer and fuels may be on the order of 10^{-4} m. In this latter situation in which reactant masses must move large distances before chemical reactions can occur, slow mass transfer rates may control the overall kinetics of the detonation reaction. . The standard detonation Chapman Jouget theory, which assumes virtually instantaneous conversion of reactants to products [1], is therefore limited in applicability to improvised explosives. Mass transfer rate limitations lead to relatively slow rates of energy release, an enhanced detonation size effect [2, 3] and greater likelihood of incomplete detonation with the possibility of further late-time oxidation of incompletely-reacted explosives with energy release (afterburn, or reaction after the detonation is complete). Current detonation theories include these effects in empirical ways that are not generally predictive, and this remains a gap in detonation science.

These effects are illustrated notionally in Figure 4 in the context of airblast from a detonation. Standard airblast theory with an instantaneously-delivered pressure pulse quite accurately described the overpressures from a detonation. [4] However, detonation with a slow reaction rate will give lower peak airblast pressures for the same energy (or impulse), and is not handled well by airblast theory. The pressure and impulse from afterburn is still more challenging from a theoretical or modeling perspective, as the pressures are much lower but the time scales much longer. As with detonation, current airblast theories include these effects in empirical ways that are not generally predictive. This is a gap in understanding of airblast and limits abilities to predict the effect of blasts from improvised explosives on structures or other target. Failure to recognize these limits may lead to incorrect analysis of target vulnerability – for example, an explosive with high afterburn energy has a very different effect than one representative of conventional detonation of the same energy, depending on the physical response time of the target.

A summary of needed improvement in theory of improvised explosives is provided in reference [5].

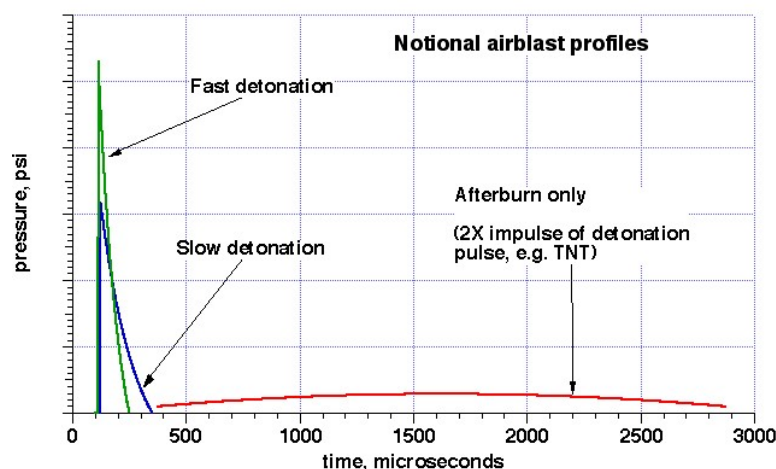


Figure 4. Notional airblast profiles illustrating energy release from improvised explosives. “Fast detonation” is for a conventional detonation. “Slow detonation” is for a detonation with 10-fold slower reaction rate, but same impulse. “Afterburn only” is for post-detonation reactions > 100-fold slower than detonations, and shows twice the impulse of the detonation curves.

3. Conventional Explosives

The behavior of conventional explosives, while much better understood than that of improvised explosives, remains challenging to understand and predict because of the complex nature of the underlying physics and chemistry. For example a simple mechanical impact on a explosive leads to localized heating and causes mechanical deformation and possibly fracturing or fragmenting of the material. If localized heating is of sufficient extent the explosive will locally ignite. The subsequent spread of that ignition and its effect on further material damage all contribute to the release of energy from the explosive. Finally, the effect of the external environment must be considered, as the presence of confinement will increase pressure and reaction rates and lead to higher reaction rates. A representation of the interplay of effects is shown in Figure 5 for mechanical and thermal insults.[6] With this picture, it is relatively straightforward to apply results from studying one or more of these steps to develop an improved integrated and predictive understanding of the overall explosive behavior. In the following sections we discuss several aspects of explosives and how they feed into the overall integrated response.

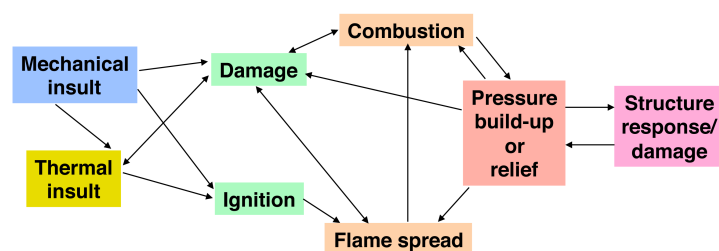


Figure 5. An integrated view of the physical and chemical processes that determine the behavior of explosives under mechanical and thermal stimuli.

3.1. Explosive crystal structure and morphology – effects on explosive behavior

The detailed processes in each step in Figure 5 are made very complex by the highly heterogeneous nature of conventional explosives. The irregular microstructures, as shown in Figure 6, provide many opportunities for localization of energy from mechanical or thermal insult. Ignition and flame spread may be highly dependent on the microstructure of the material, and the surface area available for final combustion rate will be also be governed by the explosive microstructure and the evolution of damage as the material responds to the initial stimulus.

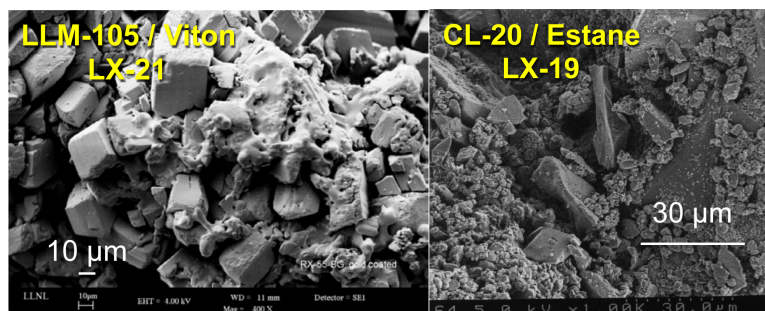


Figure 6. SEM images of two plastic bonded explosive, showing the highly heterogeneous nature. LX-21 is 94% LLM-105 and 6% Viton-A. LX-19 is 95% CL-20 and 5% Estane.

In addition to the microstructure, the crystal form of the explosive molecule plays a role in determining explosive response. Under mechanical impact, the graphitic structure of TATB as shown in Figure 7, allows the TATB crystal to slip under impact with minimal heating. In contrast, the interlocked herringbone structure of HMX leads to lattice distortion and localized heating under similar impact conditions.

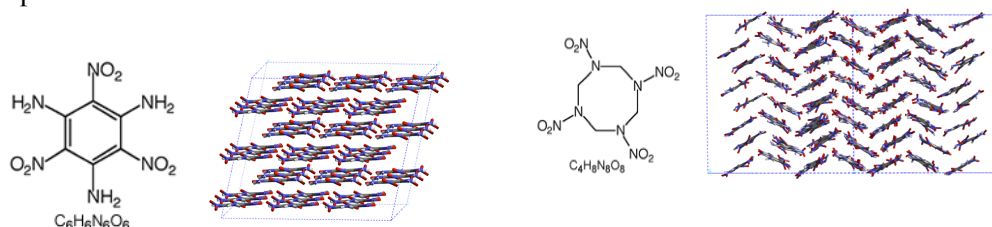


Figure 7. Molecular and crystal structure of TATB (left) and HMX (right), showing graphitic nature of TATB and herringbone structure of HMX. [7]

Explosive response to high temperature (produced locally by mechanical insult or globally by external heating) is governed by the chemical stability of the molecule. Molecule structures that enhance thermal stability, such as aromatic rings and intermolecular hydrogen bonding, lead to more stable explosives. The structures of TATB and HMX, shown in Figure 7, show that molecular structure does affect explosive stability (TATB being much less sensitive than HMX). A new explosive, LLM-105 (Figure 8), shares many of the structural attributes of TATB and is similar to TATB in its sensitivity. It is, however, not a simple graphitic structure like TATB.

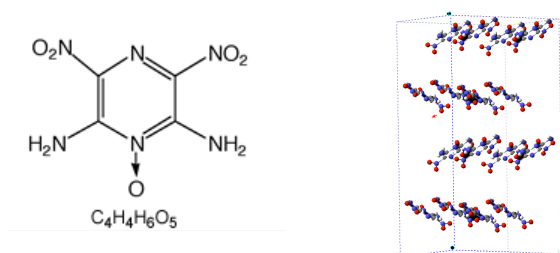


Figure 8. Molecular and crystal structure of LLM-105. [7]

3.2. The effect of damage on reaction violence

In addition to the properties of pristine explosives, the effect of external events on the explosive may strongly affect its behavior. For example, an explosive may be damaged by being exposed to a very high pressure followed by rapid depressurization. In this case the high-pressure gas apparently dissolves in the explosive and especially in the polymeric binder, and upon depressurization the evolving gas bubbles physically disrupted the sample. This is visible in the pressure cycled explosive in Figure 9, and leads to greatly-accelerated deflagration rates, with flame propagation rates 100-1000-fold higher. This is because of flame spreading along the exposed surface area instead of simply

progressing as the bulk material burns, and results in much faster energy release and pressure buildup during deflagration and increased violence of an ensuing explosion. Other mechanisms such as slow mechanical impact can also lead to exposed surface area inside the explosive and a similar increase in explosion violence.

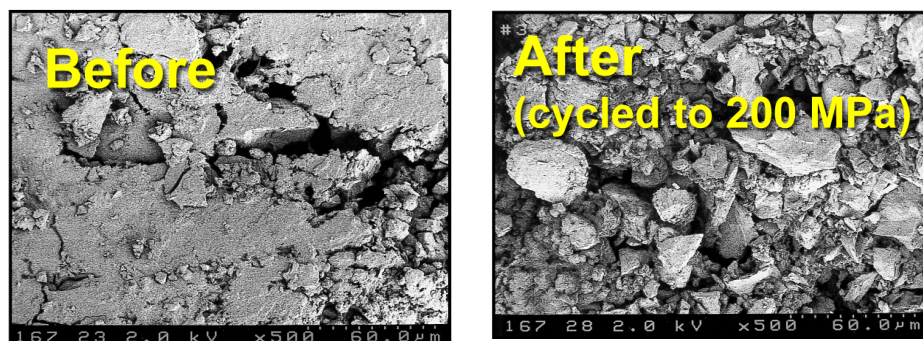


Figure 9. LX-04 (85% HMX, 15% Viton A), before and after pressure-cycling with argon.

3.3. Reactions mechanism and relevant properties

A simple mechanism of an explosive reaction is shown in Figure 10, in which the central region reacts with first an endothermic step producing fragments of the original molecule followed by a final exothermic reaction producing the final oxidized species and energy. At the same time, energy is being absorbed as latent heat in the surrounding layer and is being conducted out of the reacting volume. To the extent that the heat of reaction is retained in this central region, the reaction will be accelerated and the reaction violence will be greater. Conversely, properties that result in more energy leaving the central region (e.g., higher thermal conductivity and higher specific heat) would result in explosives with reduced reaction violence. Of course the kinetics of the chemical reactions play a dominant role, but the effect of thermo-physical properties should not be overlooked.

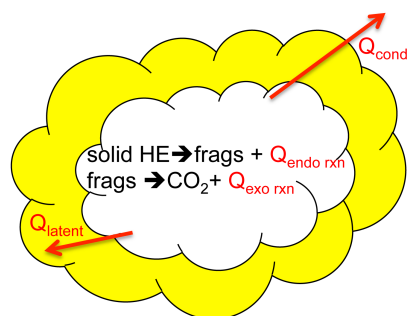


Figure 10. Simplified mechanism of explosive reaction, showing several relevant properties.

3.4. Insensitive High Explosives (IHE)

The explosive TATB and its formulation with an inert binder, Kel-F 800, are qualified as Insensitive High Explosives by the Department of Energy. This means that they are so insensitive that the probability of accidental initiation or transition from burning to detonation is negligible. [8] Comparing the properties of TATB with those of other explosives can give us insight into the nature of IHEs. Figure 11 and Table 1 below compare several properties for four explosives – HMX (conventional high explosive), ammonium picrate (conventional high explosive with improved safety properties over HMX, and of which some safety properties define threshold for IHE [8]), TATB (the one explosive molecule qualified as IHE by the DOE), and LLM-105 (a new explosive intermediate in safety between HMX and TATB [9]).

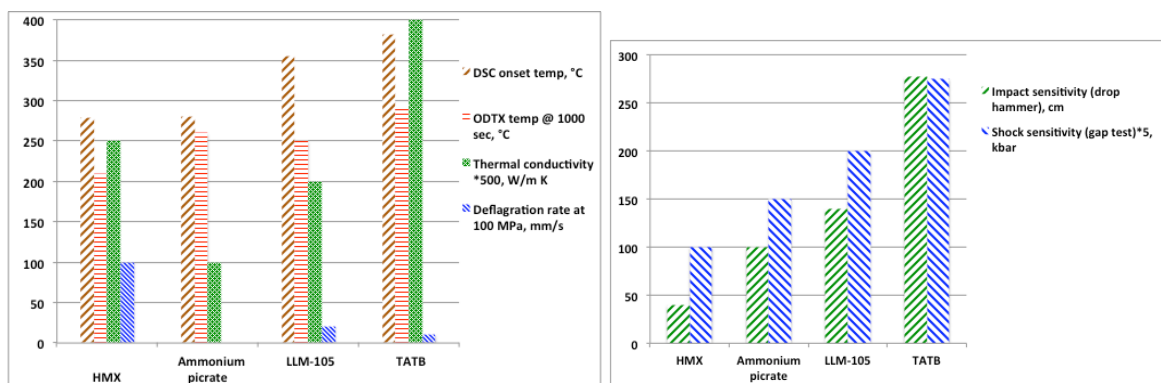


Figure 11. Comparison of properties of four explosives. Left - thermo-physical properties (note thermal conductivity values have been multiplied by 500 to fit to scale) - for first three properties, higher values lead to safer explosives, while for deflagration rate lower values lead to safer explosives. Right – impact / shock sensitivity (note shock sensitivity have been multiplied by 5 to fit to scale). [10, 11, 12]

Table 1. Comparison of qualitative properties of four explosives. Attributes that lead to safer explosives are in **bold**.

	HMX	Ammonium picrate	LLM-105	TATB
Aromatic	N	Y	Y	Y
Graphitic	N	N	N	Y
Specific heat, J/g K	1.0	1.1	0.9	1.0
P-dependent ignition	Y [13]	??	??	N
Deflagration rate pressure exponent	1+	??	1	1

The properties in Figure 11 and Table 1 can be considered in terms of explosive stability (i.e., how easy is it to start reaction) and explosive reaction rate (i.e., how rapidly the explosive releases energy once the reaction starts, determining violence of the resulting reaction). This analysis extends our earlier analysis which considered only thermal explosion violence of HMX and RDX-based explosives. [14]

Relevant properties for explosive stability include: molecular stability (aromatic structures are more stable); crystal structure (graphitic structure allows dissipation of mechanical energy by crystal shear with little frictional heating), high thermal conductivity (to dissipate energy from localized reaction sites); high specific heat (to absorb energy with smaller increase in temperature); and thermal stability (temperature needed to initiate exothermic reaction in differential scanning calorimetry (DSC) or one-dimensional time to explosion (ODTX)). From Figure 11 and Table 1 we see that the aromatic nature of ammonium picrate, LLM-105 and TATB is consistent with their being less sensitive than HMX. Only TATB is graphitic, and it is by far the most insensitive of these explosives. The thermal conductivity of TATB is significantly higher than that of the other explosives, consistent with the

above; however, the thermal conductivities of ammonium picrate and of LLM-105 are lower than that of HMX so the thermal conductivity is apparently not a strong factor in the insensitive nature of those explosives. The specific heat is approximately the same for all four explosives, so this is not a significant factor. Finally, the thermal stability indicated by the DSC onset temperature and ODTX temperature for a reaction time of 1000 seconds does track with the relative sensitivities, with HMX being the easiest to ignite, TATB being the hardest, and the others being intermediate in behavior.

Properties relevant to the explosion reaction rate include: the deflagration rate at elevated pressure (faster deflagration leading to more violent explosions); the pressure dependence of ignition (with pressure-accelerated ignition an impact leading to high pressure reduces the ignition temperature of the explosive); and the pressure dependence of the deflagration rate after ignition (deflagration accelerated by pressure increase leads to runaway reaction and explosion). From Figure 11 and Table 1 we see that the deflagration rate at 100 MPa is consistent with explosive sensitivity (TATB is very slow, HMX is very fast, and LLM-105 is in between but closer to TATB. The pressure dependence of ignition, measured by the shift in exotherm onset at different pressures, is also consistent as TATB exotherm temperature in the DSC is unchanged by high pressures while that of HMX decreases as pressure increases. Finally, the pressure exponent of the deflagration rate is unity for TATB and LLM-105; for pristine HMX the pressure exponent is also unity, but many HMX explosives exhibit a higher pressure exponent as a result of material change during the deflagration process.

Considering the above properties and interpretation of their significance, we would expect HMX to be most sensitive, TATB to be less sensitive, and ammonium picrate and LLM-105 to be somewhat in between with LLM-105 being close to TATB. That is just what is seen in the sensitivity tests in Figure 11, where the impact sensitivity and shock sensitivity are consistent with this order. Some properties remain to be determined for LLM-105, including whether its ignition temperature is dependent on pressure, but overall its properties are close to those of TATB while being a bit more sensitive. LLM-105 has not yet been tested against all the DOE requirements for an Insensitive High Explosive [8].

3.5. Predicting explosive behavior

The process of inventing new explosive molecules and developing new explosives is lengthy and somewhat Edisonian in nature. Deliberate consideration of the above properties could guide the process by focusing the development process on molecules and materials with the properties that lead to lower sensitivity. Some of the properties are inherent in the explosive molecule, and the others require only small quantities of the explosive to be measured. Pursuit of such an approach, with identification of other properties that may also play a role in determining explosive sensitivity, could significantly accelerate the development of new explosives to meet modern safety requirements.

4. Conclusions

We have compared the behaviors of many different explosives in the context of the chemical and physical properties of the materials. For improvised explosives, behaviors are dominated by the unusual nature of the materials, often as physical mixtures, with widely-varying reaction mechanisms and energy-release rates. Understanding of these improvised explosives requires development of insight into these processes. For conventional explosives, the behavior in response to accidental or deliberate stimuli is controlled by a set of molecular and thermophysical and thermochemical properties and the interaction of the many mechanistic steps controlled by these properties. We have identified a set of underlying mechanistic steps in determining explosive behavior and shown how they interact. In addition, we presented a set of relevant properties with discussion of their impact on explosive behavior.

We expect there are other properties that are also relevant to this discussion, and look forward to their identification and elucidation. Improved understanding of properties underlying explosive behaviors will accelerate the development of new materials to address modern safety needs. In addition, as the ability to convert mechanistic understanding into predictive computer models matures [6, 15], we expect modeling to provide further guidance to development of new explosive molecules and mixtures.

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